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Derwent Online Abstract, WPI accession no 81-65092D/36 (& JP 56/090004 [1981])

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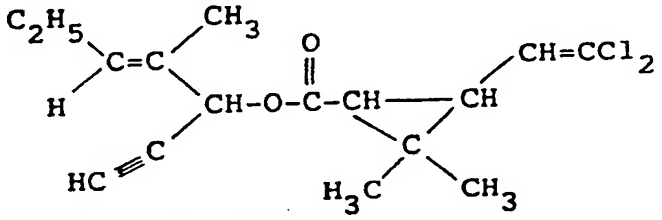
Online databases: CAS ONLINE

(54) Method for controlling insects and/or acarines by vaporising a pyrethroid in the absence of heating

(57) A method for controlling insects and/or acarines comprises vaporizing 1-ethynyl-2-methyl-2-pentenyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate having the formula,



[I]

without heating it, ie at a temperature in the range 0-30°C.

In contrast with conventional methods, the method of the present invention is useful for controlling insects and/or acarines not only in a narrow space but also in a wider space, such as a room, storage chamber, closet, warehouse, vehicle, ship, airplane, store, cattle shed, stable, drainage trench or sewer for a long period of time.

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METHOD FOR CONTROLLING INSECTS AND/OR ACARINES

The present invention relates to a method for controlling insects and/or acarines which comprises vaporizing an active ingredient without heating the same.

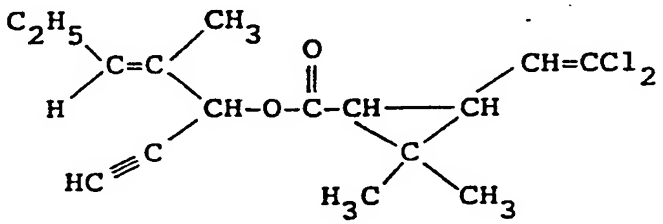
Although various insecticidal and/or acaricidal agents are known today, organophosphorus insecticides such as dichlorvos ($(CH_3O)_2PO{\cdot}OCH{=}CCl_2$) may be an isolated instance for the agents suited for a method for controlling insects and/or acarines comprising vaporizing an active ingredient without actually heating. As a sole instance for such a method with a pyrethroid compound, an insecticide of low toxicity, there has been reduced to practice a method comprising vaporizing 1-ethynyl-2-methyl-2-pentenyl chrysanthemate for controlling pests injurious to clothing.

When used in a relatively narrow space such as a chest of drawers, a drawer, etc., 1-ethynyl-2-methyl-2-pentenyl chrysanthemate is effective in controlling pests injurious to clothing. However, unless used in a considerably large amount, this agent is not necessarily effective in controlling pests in a wide space such as room, storage chamber, closet, ware-house, vehicle, ship, airplane, store, cattle shed, stable, drainage trench, sewer, etc. Also for duration of the activity for a long period of time, the agent should be used in a large amount.

Vaporization of an active ingredient by heating

is sometimes effective in enhancing the initial efficacy. But, saving in energy is required for protecting the earth environment. If an active ingredient can be vaporized without heating, it will become possible to save precious energy. Moreover, there can be prevented dangers of burning and fire due to a heating element or heat generator for vaporizing the active ingredient.

According to the present invention, there is provided a method for controlling insects and/or acarines comprising vaporizing 1-ethynyl-2-methyl-2-pentenyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (hereinafter Compound I) having the formula,



[I]

without heating the same.

The present inventors earnestly investigated a method for effectively controlling insects and/or acarines comprising vaporizing an active ingredient without heating, and consequently found that out of numerous well-known insecticidal and acaricidal agents, Compound I is the most suitable for the object of the present invention, whereby the present invention was accomplished.

It has been disclosed in JP-B-55-42045 that

Compound I has an insecticidal and acaricidal activity. The present inventors, however, found that mere vaporization of said compound without heating exhibits a high initial activity against insects and/or acarines and that the activity lasts for a long period of time, whereby the present inventors were led to the present invention.

The term "without heating" used herein means at an ordinary temperature (without heating or cooling), namely, at a temperature not higher than 30°C but higher than about 0°C.

The method of the present invention is effective against various insect pests and acarine pests. It is markedly effective against hygienic pests, wood pests, food stuff pests, household nuisance pests, etc. Particularly, it is most effective against hygienic pests and household nuisance pests.

Specific examples of insect pests and acarine pests to which the method of the present invention can be applied are given below.

Lepidoptera

Plodia interpunctella (Indian meal moth), etc.

Diptera

Culex spp. (common mosquitoes), Anopheles spp. (Anopheline mosquitoes), Aedes spp., Muscidae (house flies), Drosophilidae (wine flies), Psychodidae (moth flies), Chironomidae (chironomid midges), Calliphoridae (blow flies), Sarcophagidae (flesh flies), Simuliidae (black flies), Tabanidae (tabanid flies), Stomoxyidae

(stable flies), etc.

Coleoptera

Sitophilus zeamais (maize weevil), *Callosobruchus chinensis* (adzuki bean weevil), *Tribolium castaneum* (red flour beetle), Anobiidae (deathwatch and drugstore beetles), Lyctidae (powder post beetles), *Paederus fuscipes* (robe beetle) etc.

Dictyoptera

Blattella germanica (German cockroach), *Periplaneta fuliginosa* (smokybrown cockroach), *Periplaneta americana* (American cockroach), *Periplaneta brunnea* (brown cockroach), *Blatta orientalis* (oriental cockroach), etc.

Hymenoptera

Formicidae (ants), Bethylidae (bethylid wasps), etc.

Siphonaptera

Pulex irritans, etc.

Anoplura

Pediculus humanus capitis (body louse), *Pthirus pubis* (crab louse), etc.

Isoptera

Reticulitermes speratus, *Coptotermes formosanus* (Formosan subterranean termite), etc.

Acarina

Mites associated with house dust and stored food, such as Acaridae, Pyroglyphidae, Cheyletidae, and the like, Ixodidae such as *Boophilus microplus*, and the like, Dermanyssidae, etc.

For controlling insects and/or acarines by vaporizing Compound I, a carrier is not always necessary. Usually, Compound I is used after being supported on a suitable carrier.

Specific examples of the carriers for adsorption of Compound I are papers such as filter paper, cardboard and the like; pulp; plastic resins such as polyethylene, polypropylene, vinyl chloride and the like; ceramics; asbestos; glass fiber; carbon fiber; chemical fibers; natural fibers; nonwoven fabrics; substrates for fumigating mat (a plate formed of fibril of a mixture of cotton linter and pulp); porous polymer films; porous glass materials; metal plates (e.g. aluminum dish); etc. These carriers which have Compound I supported thereon can be used in any preparation form. In the case plastic resins are used as a carrier, the plasticity of the preparation can be improved by blending therein a plasticizer such as dioctylphthalate.

However, a carrier is not always necessary. When there is any article made of the above material in a room in which insects or acarines, or both, are to be controlled, it is sufficient that Compound I is supported on the article.

The vaporizing efficiency can be further increased by adding subliming materials such as adamantane, cyclododecane, trimethylnorbornane, etc., as adjuvant for promoting the vaporization.

It is also possible to enhance the efficacy by using Compound I in admixture with known synergists

effective for allethrin and pyrethrins, etc., specific examples of which being synergists for pyrethroid such as α-[2-(2-butoxyethoxy)ethoxy]-4,5-methylenedioxy-2-propyltoluene (piperonyl butoxide), N-(2-ethylhexyl)-bicyclo[2,2,1]hepta-5-ene-2,3-dicarboxyimide (MGK-264 ®), octachlorodiisopropyl ether (S-421 ®), Synepirin-500 ®, etc.

The activity of Compound I can be stabilized by using Compound I as a blend with an antioxidant and an ultraviolet absorber for increasing the stability to light, heat, oxidation, etc. Specific examples of the antioxidant are 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,6-di-tert-butyl-4-methylphenol (BHT), 2,6-di-tert-butylphenol, 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-butylidenebis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), and dibutylhydroquinone (DBH). The specific examples of the ultraviolet absorber are phenol derivatives such as BHT, bisphenol derivatives, arylamines such as condensation products between phenyl-α-naphthylamine, phenyl-β-naphthylamine or phenetidine and acetone, and benzophenone compounds.

Compound I may be used in admixture with dyes such as allylaminoanthraquinone, 1,4-diisopropylamino-anthraquinone, 1,4-diaminoanthraquinone, 1,4-dibutyl-aminoanthraquinone, 1-amino-4-anilinoanthraquinone and the like, and perfumes for vaporizable composition.

In supporting Compound I on a carrier, there can, if necessary, be used additives such as fatty acid esters (e.g. isopropyl myristate, isopropyl palmitate and hexyl laurate) and organic solvents (e.g. isopropyl alcohol, polyethylene glycol and deodorized kerosine) in order to lower the viscosity and facilitate impregnation.

The carrier having Compound I supported thereon which is obtained in the manner described above can be used as it is by allowing Compound I to vaporize without heating. It exhibits a high insecticidal and/or acaricidal activity when placed not only in a narrow space but also in a wider space such as a room, storage chamber, closet, warehouse, vehicle, ship, airplane, store, cattle shed, stable, drainage trench, sewer, etc.

In the method of the present invention, the application rate of Compound I is not critical. It should be determined in view of many factors such as the concentration of Compound I, type of formulations, manner and timing of application, environmental temperature and humidity, space to be applied and the width thereof, whether the space is open or not, whether natural or artificial air streams go through the space or not, kind of insects or acarines to be controlled, habitat of insects or acarines, etc. However, Compound I is usually applied in a ratio of from 1 mg/m^3 to 500 g/m^3, preferably 10 mg/m^3 to 5 g/m^3. This is only a rough standard and Compound I may be applied beyond the range as occasion demands.

Forming an air stream by stirring the air by artificial wind from a motorized fan (e.g. an electric fan) or from an air-conditioner or by natural wind may encourage the insecticidal and/or acaricidal efficacy of the method of the present invention so as to enable to apply the method in a wider space.

Compound I can be prepared according to the process disclosed in JP-B-55-42045, for example.

Compound I has optical isomers due to the asymmetric carbon atoms in the alcohol moiety and the acid moiety. It also has geometrical isomers due to the cyclopropane ring in the acid moiety. Some of them are shown in Table 1. Of the isomers, Compounds [I]-A, [I]-B and [I]-C are more active than the other isomers.

Table 1

Symbol of compound	Configuration of the alcohol moiety	Configuration of the acid moiety
[I]-A	S	1R-trans
[I]-B	S	1RS-trans
[I]-C	RS	1R-trans
[I]-D	RS	1RS-cis
[I]-E	RS	1RS-cis,trans

The following reference example, formulation examples and test examples serve to give specific illustration of the present invention but they are not intended in any way to limit the scope of the present invention.

Reference Example

Compound [I]-A was prepared as follows:

0.50 Grams of (1S)-1-ethynyl-2-methyl-2-pentenol (described in JP-B-63-52615) was dissolved in dry toluene, and 0.50 g of pyridine was added thereto. To the resulting solution was added 0.90 g of (1R)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid chloride (the corresponding carboxylic acid is described in JP-A-62-253398, for example). The resulting solution was stirred overnight at room temperature. The reaction mixture, after water had been added thereto, was extracted with toluene. The organic layer was washed successively with dilute aqueous hydrochloric acid, saturated aqueous solution of sodium hydrogen carbonate and saturated aqueous solution of sodium chloride. Thereafter, the layer was dried over anhydrous sodium sulfate. The dried layer was filtered and concentrated to obtain a residue. Purifying the residue with silica gel chromatography (eluent: a 10:1 mixture of hexane and ethyl acetate) gave 1.05 g of (1S)-1-ethynyl-2-methyl-2-pentenyl (1R)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (Compound [I]-A) in a yield of 83%.

$n_D^{20.5}$: 1.5063

$[\alpha]_D^{24}$: -7.2° (dimethyl ether, C=0.53)

Formulation Example 1

In an adequate amount of acetone was dissolved 100 mg of Compound I. The solution was uniformly coated on a filter paper having an area of 10 cm square and a thickness of 0.3 cm. Air-drying the paper to remove acetone therefrom gave a composition capable of vaporizing the active ingredient without heating (hereinafter a non-heating type vaporizable preparation).

Formulation Example 2

In an adequate amount of acetone were dissolved 200 mg of Compound I and 100 mg of BHT. The solution was uniformly coated on a filter paper having an area of 10 cm x 15 cm and a thickness of 0.3 cm. Air-drying the paper to remove acetone therefrom gave a non-heating type vaporizable preparation.

Formulation Example 3

In an adequate amount of acetone was dissolved 600 mg of Compound I, and a 10 cm x 15 cm filter paper was allowed to absorb the resulting solution uniformly. Air-drying the paper to remove acetone therefrom gave a non-heating type vaporizable preparation.

Formulation Example 4

In an adequate amount of acetone was dissolved 200 mg of Compound I. The solution was poured into an aluminum dish having an inner diameter of 9 cm so that the solution was spread uniformly in the bottom. Air-drying the dish to remove acetone therefrom gave a non-heating type vaporizable preparation.

Formulation Example 5

250 Milligrams of Compound I and 250 mg of polyethylene glycol were dissolved in an adequate amount of acetone. With the mixture was uniformly impregnated a substrate for fumigating mat (a plate formed of fibril of a mixture of cotton linter and pulp) having a size of 10 cm x 30 cm and a thickness of 0.28 cm. Air drying the mat to remove acetone therefrom gave a non-heating type vaporizable preparation.

Formulation Example 6

65 Parts by weight of powdery polyvinyl chloride are admixed with 30 parts by weight of dioctylphthalate as a plasticizer. The mixture is heat-melted at 150°C. To this thermoplastic resin is blended 5 parts by weight of Compound I, and the resulting mixture is well kneaded in a closed system. The kneaded mixture is injection-molded into a plate having a size of 5 cm x 6.5 cm and a thickness of 0.5 cm and cooled to obtain a non-heating type vaporizable preparation.

In the following test examples, the members tested of Compound I are indicated by the symbols shown in Table 1, and the compounds used for comparison are indicated by the symbols shown in Table 2.

Table 2

Symbol of compound	Chemical name	Remarks
(A)	(RS)-3-allyl-2-methyl-4-oxocyclopent-2-enyl (1R)-trans-chrysanthemate	bioallethrin
(B)	(RS)-1-ethynyl-2-methyl-2-pentenyl (1R)-cis,trans-chrysanthemate	empenthrin
(C)	2,2-Dichlorovinyl dimethylphosphate	dichlorvos

Test Example 1

The following test was carried out using an aluminum dish obtained according to Formulation Example 4. The amount of active ingredient was adjusted to 0.005 mg/aluminum dish.

Twenty female adult houseflies (Musca Domestica, CSMA-strain) were released in a polyethylene cup (diameter: 9 cm, height: 4.5 cm). Then, the upper part of the cup was covered with a 16-mesh nylon net. The cup was closed with the aforesaid aluminum dish so that the agent-treated surface of the dish might face the inside of

the cup. The nylon net was for preventing direct contact of the insects with the agent-adhered surface. After the lapse of 120 minutes at 27°C, the aluminum dish was removed and water and diet were given to the insects. After 24 hours, the dead and alive were counted for mortality (two replications).

Table 3 shows the results.

Table 3

Compound tested	Mortality (%)
[I]-A	100
[I]-B	100
[I]-C	100
(A)	0
(B)	2.5
(C)	5
Untreated	2.5

Test Example 2

A filter paper preparation obtained according to Formulation Example 1 except for changing the amount of the active ingredient to 3.4 mg/filter paper, was suspended in a glass chamber of 0.34 m^3 (70 cm cube) in midair with a string having a length of 10 cm from the center of the ceiling of the glass chamber. The amount used of the active ingredient per unit space was 10

1 mg/m^3. The room temperature was 25°C.

After the lapse of 30 minutes, 20 female adult common mosquitoes (Culex pipiens pallens) were released in the chamber. 60 Minutes after releasing the insects, the
5 knocked-down insects were counted for percentage of knocked-down insects. (two replications).

Table 4 shows the results.

Table 4

Compound tested	Knocked-down (%)
[I]-A	100
[I]-B	100
[I]-C	100
(A)	0
(B)	55
(C)	65
Untreated	0

Test Example 3

A filter paper preparation obtained according to
10 Formulation Example 3 was cut up into six equal pieces having a size of 5 cm x 5 cm (amount of active ingredient: 100 mg/piece of filter paper).

Twenty adults of Tyrophagus putrescentiae were placed in a glass Petri dish having a diameter of 9 cm and
15 a height of 2 cm together with diet. Then the mouth of

the Petri dish was covered with a 16-mesh nylon net. The aforesaid filter paper piece was placed on the nylon net, and the Petri dish was closed with another Petri dish having the same size. The assembly thus obtained was allowed to stand at room temperature (30°C) and at a humidity of 75%. After 24 hours, the dead and alive were counted for mortality. (two replications).

Table 5 shows the results.

Table 5

Compound tested	Mortality (%)
[I]-A	100
[I]-B	100
[I]-C	100
Untreated	7.5

Test Example 4

Residual activity test was carried out as follows with a substrate for fumigating mat prepared according to Formulation Example 5 (the amount of active ingredient: 250 mg/mat).

In a Peet Grady's chamber of 6.1 m^3 (183 cm cube), the mat was suspended in midair with a string having a length of 20 cm from the center of the ceiling. Then, the mat was left suspended for 9 hours at room temperature (25°C). The amount used of active ingredient

per unit space was 41 mg/m^3. Nine hours later, 100 adult houseflies (Musca domestica) were released in the chamber. The number of houseflies knocked down in 30 minutes was counted for percentage of knocked down insects.

After the test, the mat was taken from the chamber. It was suspended with a cord in midair in a corrugated cardboard box (size: 30 cm x 28 cm, height: 36 cm). The box was allowed to stand in a room at 25°C.

The same test was repeated with the mat stored in the corrugated cardboard box for 1, 3, 5, 8 and 12 weeks after the initial test. Table 6 shows the results.

Table 6

Compound tested	Knocked-down (%)					
	Initial	After 1 week	After 3 weeks	After 5 weeks	After 8 weeks	After 12 weeks
[I]-A	100	100	100	100	100	100
(A)	0	3	1	3	2	2
(B)	100	100	100	80	42	22
(C)	100	100	76	44	19	3
Untreated	0	2	1	3	0	1

WHAT IS CLAIMED IS:

1. A method for controlling insects and/or acarines comprising vaporizing 1-ethynyl-2-methyl-2-pentenyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate without heating the same.

2. A method for controlling insects and/or acarines comprising vaporizing 1-ethynyl-2-methyl-2-pentenyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate at 0° to 30°C.

3. A method for controlling insects and/or acarines comprising vaporizing (1S)-1-ethynyl-2-methyl-2-pentenyl (1R)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate without heating the same.

4. A method for controlling insects and/or acarines comprising vaporizing (1S)-1-ethynyl-2-methyl-2-pentenyl (1R)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate at 0° to 30°C.

5. A method for controlling insects and/or acarines comprising vaporizing (1S)-1-ethynyl-2-methyl-2-pentenyl (1RS)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate without heating the same.

6. A method for controlling insects and/or acarines comprising vaporizing (1S)-1-ethynyl-2-methyl-2-pentenyl (1RS)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate at 0° to 30°C.

7. A method for controlling insects and/or acarines comprising vaporizing (1RS)-1-ethynyl-2-methyl-2-pentenyl (1R)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclo-

propanecarboxylate without heating the same.

8. A method for controlling insects and/or acarines comprising vaporizing (1RS)-1-ethynyl-2-methyl-2-pentenyl (1R)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate at 0° to 30°C.

9. A method according to any preceding claim substantially as herein described and exemplified.